

A thermodynamic theory of solid viscoelasticity. Part II: Nonlinear thermo-viscoelasticity

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Abstract

This paper, second in the series of three papers, develops a general, nonlinear, non-isothermal, compressible theory for finite rubber viscoelasticity and specifies it in a form² convenient for solving problems important to the rubber, tire, automobile, and air-space industries, among others. Based on the quasi-linear approach of non-equilibrium thermodynamics, a general nonlinear theory of differential type has been developed for arbitrary non-isothermal deformations of viscoelastic solids. In this theory, the constitutive equations were presented as the sum of a rubber elastic (equilibrium) and a liquid type viscoelastic (non-equilibrium) terms. These equations have then been simplified using several modeling and simplicity arguments.

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1. Introduction

Noll, Coleman, Truesdell, and their followers developed a general nonlinear theory they called the rational mechanics (e.g. see Truesdell and Noll, 1992). which searched for the most general forms of constitutive equations (CE's). The basic set involving constitutive and thermodynamic equations was constructed there with a mathematical rigorosity; the constitutive equations satisfy: the general principles of causality, material objectivity and locality. Using this approach, they attempted to generally describe the properties of viscoelastic liquids by a set of hereditary functionals with fading memory, whose invariance properties and thermodynamic consistency were perfectly revealed. This approach could also be easily extended for viscoelastic solids. Unfortunately, the memory functionals in the rational mechanics have never been specified, and more importantly, it is unknown (if possible) how to do that. Therefore in spite of many achievements, the general rational mechanics and thermodynamics theories seem to be useless for predicting behavior of real materials.

Two less general continuum approaches to nonlinear viscoelastic CE's have been suggested for applications. One is the K-BKZ single-integral approach, independently developed by Kaye (1962) and Berstain, Kersley, Zapas (1963), which is applicable for both viscoelastic liquids and solids (see also, Larson, 1988). Another approach is of differential type (Leonov, 1976, 1987, 1999) developed for viscoelastic liquids using non-equilibrium thermodynamics (see also Sidoroff, 1974, and historical remarks in Leonov, 1976,1987). Both of these approaches are considered below and are considered as complementary in applications to viscoelastic solids, mostly for solid polymers, or being more precisely, for the thermo-mechanical properties of cross-linked rubbers.

The relaxation phenomena, which are not taken into account in theories of pure elastic solids, enhance the complexity of problems for polymers. Hence, polymer solids demonstrate many nonlinear viscoelastic effects, such as nonlinear creep and relaxation, hysteresis etc., which are not seen in the other solids. Because of these complications, even geometrically simple problems that are solvable analytically for elastic solids have to be treated numerically in the viscoelastic case.

There are practical needs for developing a thermodynamically based theoretical approach to solid nonlinear viscoelasticity, which might be valid for a wide range of strains, strain rates (frequencies) and temperatures. It seems that this approach should combine (i) a nonlinear multi-mode CE of differential type generated by that part of a relaxation spectrum with high relaxation times, and (ii) a nonlinear single-integral CE generated by that part of a relaxation spectrum with low relaxation times. We assume that both parts of the combined CE are almost independent, with part (i) working for relatively slow motions of continuum unddergoing very large strains and having WLF time-temperature superposition principle appropriate for relatively high temperatures at the rubbery states, and with part (ii) working for fast (and very fast) motions of the continuum undegoing relatively small (and very small) strains and another time-temperature scaling valid for glassy state. Thus this approach will take into account thermo-rheological complexity along with high non-linearities of elastic and viscoelastic deformations, including compressibility effects. In this paper, only the first part of the above proposal, the part (i) of the CE's, is demonstrated.

In models of the differential type designed for description of viscoelastic solids like cross-linked rubbers, the typical nonlinear pure elastic term should be included along with differential modes, originated from linear (Prony) viscoelastic modes with different and usually well-separated relaxation times. The simple assumption is that this term is additive to the viscoelastic ones. This assumption has been used by Reese and Govindjee (1997) and Bergstrom and Boyce (1998), for example, where the only nonlinear extension of the “standard” (three-parametric) linear viscoelastic solid model has been employed. The treatment of the dissipative term in the evolution equation used by Reese and Govindjee (1997) for a nonlinear Maxwell element is not convincing, and the whole approach to the evolution equation for this element developed by Bergstrom and Boyce (1998) is questionable. An additional important question to ask of the paper by Bergstrom and Boyce (1998), where both the pure gum elastomers and carbon black filled compounds were studied, relates to their treatment of Mullins hysteresis for carbon black filled rubbers as a pure relaxation effect. It is, however, known (see Joshi and Leonov, 2001) that this effect, being structurally reversible (i.e. thixotropic), is not of a type that originates from relaxations of an elastomer matrix. It usually takes several months at room temperature for the complete recovery of a filled elastomer under unloading.

The differential type of modeling has another importance: one can establish the transformation in behavior from liquid to solid-like via vulcanization using chemorheological modeling (Mitra, 2000) with this type of CE. Surprisingly, for filled elastomer compounds, this type of modeling was done first by Joshi and Leonov (2001).

Other nonlinear viscoelastic models of a differential type have also been recently proposed in the literature, being based on pure continuum mechanical phenomenology. For example, Saleeb and Arnold (2001) (see also the references cited therein) developed such an approach that also includes some nonlinear elements, modeling plasticity with the von-Mises type yield criterion. Also, Huber and Tsakmakis (2000) attempted to extend on arbitrarily nonlinear case of the linear, 3-parametric, “standard”, solid viscoelastic model with two equivalent designs using two springs and one dashpot. These two nonlinear models are presented in an awkward form, based on separating the total viscoelastic strain in a product of elastic and inelastic components, along with use of the second law. Recently Lin (2000) introduced another approach, which is close in spirit to that elaborated in the present paper. It analyzes viscoelastic solids in terms of a separate set of nonlinear Maxwell modes (with hidden tensor parameters) added to the equilibrium elastic mode. Although the equilibrium mode has been treated in a general and correct way, the evolution equations for the Maxwell modes as written violate material objectivity, and the dissipation term was proposed to be similar to the stress in the Maxwell mode, i.e. without strain-induced anisotropy. The same defects in analyzing the viscoelastic evolution equation in a model designed for finite deformations of viscoelastic solids, extended from the three-parametric, “standard” solid, viscoelastic model, can also be seen in papers by Bergstrom and Boyce (1998,1999,2000), in a recent review by Boyce and Arruda (2000), and in the work by Huang (1999).

The first step in developing practically useful nonlinear, multi-modal, differential models for viscoelastic solids is the elaboration of reliable methods for determining linear relaxation spectrum, which remains valid for thermo-rheological complexity over a large region of temperatures and frequencies. A thermodynamic theory for linear viscoelastic phenomena with thermo-rheological complexity has been developed by Freed and

Leonov (2002) in the previous paper of this series, where the Pade-Laplace method developed by Simhabhatla and Leonov (1993) for determining the spectrum from experimental data has also been discussed.

The structure of the present paper is as follows. We initially develop a general, non-linear constitutive theory for general non-isothermal and compressible elastic and viscoelastic behavior of rubber-like solids, with a single nonlinear relaxation mode. In this, we follow the thermodynamic approach (Leonov, 1976, 1987, 1999) developed for nonlinear liquid-like viscoelasticity. Then we simplify this theory and extend it for the multi-mode case, along with a simplified fractioning of compressible and incompressible effects in nonlinear elasticity and viscoelasticity.

2. A nonlinear theory of solid viscoelasticity with a single relaxation mode

2.1. State variables and free energy

We employ in this Section the general approach of irreversible thermodynamics discussed in various books (e.g. see de Groot and Mazur, 1962). We assume that in the simple case under study, the state variables for a viscoelastic solid are: the temperature T , a measure of total strain, say, the Finger deformation tensor $\underline{\underline{B}}$, and a hidden variable $\underline{\underline{b}}$, assumed to be a symmetric second-rank non-dimensional tensor. We also assume that tensor $\underline{\underline{b}}$ is positive definite which, to some extent, can be justified (e.g. see Leonov, 1987, 1999). Tensor $\underline{\underline{b}}$ is treated below as the Finger deformation for elastic (recoverable) strain, which can sometimes be independently measured. It is expected that introducing tensor $\underline{\underline{b}}$ into the set of state variables will lead to a nonlinear relaxation mechanism, which hopefully can properly describe nonlinear relaxation phenomena observed in cross-linked rubbers. In the following, we employ the Eulerian formulation of CE's and, without loss of generality, use a Cartesian coordinate system for their description.

It is convenient to introduce the Helmholtz' free energy density F per mass unit as a proper thermodynamic potential, that depends on temperature T and the basic invariants of tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$. The crucial simplifying assumption that underlies all of today's approaches is that the free energy might be represented as a sum of two contributions, one from equilibrium processes (with tensor $\underline{\underline{B}}$ as its parameter), and another from non-equilibrium processes (with tensor $\underline{\underline{b}}$ as its parameter):

$$F \approx F^0(T; I_1^B, I_2^B, I_3^B) + F^1(T; I_1, I_2, I_3), \quad (1)$$

with no coupling present between $\underline{\underline{B}}$ and $\underline{\underline{b}}$. Although the fractioning (1) of the free energy in the a of equilibrium and non-equilibrium terms is unnecessary for developing the formal approach demonstrated below, it is one of simplifying assumptions we finally use to make the approach useful for practical applications.

The variables I_j^B and I_j in (1) are the tensor invariants of $\underline{\underline{B}}$ and $\underline{\underline{b}}$ that arise from the Hamilton-Cayley theorem, which are:

$$\begin{aligned}
I_1^B &= \text{tr} \underline{\underline{B}}, \quad I_2^B = 1/2[(I_1^B)^2 - \text{tr} \underline{\underline{B}}^2], \quad I_3^B = \det \underline{\underline{B}}; \\
I_1 &= \text{tr} \underline{\underline{b}}, \quad I_2 = 1/2(I_1^2 - \text{tr} \underline{\underline{b}}^2), \quad I_3 = \det \underline{\underline{b}}
\end{aligned}
\tag{2}$$

A “thermodynamic” stress tensor $\underline{\underline{\sigma}}^T$ associated with the free energy F can be defined as:

$$\underline{\underline{\sigma}}^T = \underline{\underline{\sigma}}_0 + \underline{\underline{\sigma}}_1. \tag{3}$$

Here $\underline{\underline{\sigma}}_0$ and $\underline{\underline{\sigma}}_1$ are respectively the equilibrium and non-equilibrium parts of the total thermodynamic (Cauchy) stress tensor. These parts are presented as follows:

$$\underline{\underline{\sigma}}_0 = 2\rho \underline{\underline{B}} \cdot \partial F^0 / \partial \underline{\underline{B}} = 2\rho [F_1^0 \underline{\underline{B}} + F_2^0 (I_1^B \underline{\underline{B}} - \underline{\underline{B}}^2) + F_3^0 I_3^B \underline{\underline{\delta}}] \quad (F_j^0 = \partial F^0 / \partial I_j^B) \tag{4}$$

$$\underline{\underline{\sigma}}_1 = 2\rho \underline{\underline{b}} \cdot \partial F^1 / \partial \underline{\underline{b}} = 2\rho [F_1^1 \underline{\underline{b}} + F_2^1 (I_1 \underline{\underline{b}} - \underline{\underline{b}}^2) + F_3^1 I_3 \underline{\underline{\delta}}]. \quad (F_j^1 = \partial F^1 / \partial I_j)$$

In (3) and (4), ρ is the mass density, $\underline{\underline{\delta}}$ is the unit tensor, $\underline{\underline{\sigma}}_0$ and $\underline{\underline{\sigma}}_1$ are pure elastic (equilibrium) and viscoelastic (quasi-equilibrium) stresses, respectively. The only physical reason to use the suggested form in the second equation (4) is the explicit assumption (Leonov 1976, 1987, 1999) that polymeric liquids and solids always possess an “instantaneous” elastic limit, a quasi-equilibrium situation achieved on very fast (instantaneous) deformations, where the temporary entanglements in macromolecules act like additional cross-links. Note that no incompressibility assumption has been made.

We further use the well-known kinematical relation for Finger deformation $\underline{\underline{B}}$:

$$\overset{\nabla}{\underline{\underline{B}}} \equiv \overset{\nabla}{\underline{\underline{B}}} - \underline{\underline{B}} \cdot \underline{\underline{e}} - \underline{\underline{e}} \cdot \underline{\underline{B}} = \underline{\underline{0}}. \tag{5}$$

Here $\overset{\nabla}{\underline{\underline{B}}}$ and $\overset{0}{\underline{\underline{B}}}$ are upper-convected and corotational (Jaumann) tensor time derivatives, and $\underline{\underline{e}}$ is the strain-rate (or rate of deformation) tensor. The corresponding kinematical (or kinetic) equation describing the evolution of tensor $\underline{\underline{b}}$, the main goal of the following constitutive theory, has yet to be established.

2.2. Entropy production and nonlinear, non-isothermal relaxations

The dissipative effects that have already been analyzed in detail for viscoelastic liquids in (Leonov, 1976, 1987, 1999) are now applied to viscoelastic solids with their non-steady, i.e. time dependent deformations. In order to describe the dissipative effects we use the continuum form of the Clausius-Duhem expression for the entropy production P_s , which in the general case under study has the form:

$$TP_s = -\underline{\underline{q}} \cdot \underline{\underline{\nabla}} T + \text{tr}(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - \rho dF/dt|_T \geq 0 \tag{6}$$

The second and third terms on the right-hand side of (6), which can be presented in the form $D \equiv TP_s|_T$, are called the mechanical dissipation. First we consider the isothermal behavior of viscoelastic solids. Equations (4)-(6) allow identically rewrite the dissipation in (6) as follows:

$$\begin{aligned} D \equiv TP_s|_T &= tr(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - \rho dF/dt|_T \\ &= tr(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}) - tr(\underline{\underline{\sigma}}_0 \cdot \underline{\underline{B}}^{-1} \cdot 1/2 \overset{0}{\underline{\underline{B}}}) - tr(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{b}}^{-1} \cdot 1/2 \overset{0}{\underline{\underline{b}}}) = tr[(\underline{\underline{\sigma}} - \underline{\underline{\sigma}}_0) \cdot \underline{\underline{e}}] - tr(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{b}}^{-1} \cdot 1/2 \overset{0}{\underline{\underline{b}}}) \end{aligned} \quad (7)$$

The next step in the development of our theory is the introduction of an evolution law for tensor $\underline{\underline{b}}$, similar to the kinematical equation (5). This has been discussed elsewhere (Leonov, 1976,1999) and resulted in the definition of “thermodynamic flux”, the tensor $\underline{\underline{e}}_e$:

$$\overset{0}{\underline{\underline{b}}} - \underline{\underline{b}} \cdot \underline{\underline{e}}_e - \underline{\underline{e}}_e \cdot \underline{\underline{b}} = \underline{\underline{0}}. \quad (8)$$

Inserting (8) into (7) yields:

$$D = tr[(\underline{\underline{\sigma}} - \underline{\underline{\sigma}}_0) \cdot \underline{\underline{e}}] - tr(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{e}}_e). \quad (9)$$

Note that in the equilibrium limit, $\underline{\underline{b}} \rightarrow \underline{\underline{B}}$ (and correspondingly, $\underline{\underline{e}}_e \rightarrow \underline{\underline{e}}$), equation (8) coincides with (5). It is also seen from (5) that $\underline{\underline{\sigma}}_1 \rightarrow \underline{\underline{\sigma}}_0$ when $\underline{\underline{b}} \rightarrow \underline{\underline{B}}$. It is therefore convenient to introduce the pure non-equilibrium (dissipative) quantities, the stress $\underline{\underline{\sigma}}_p$ and strain rate $\underline{\underline{e}}_p$, both of which vanish in equilibrium:

$$\underline{\underline{\sigma}}_p \equiv \underline{\underline{\sigma}} - \underline{\underline{\sigma}}^T = \underline{\underline{\sigma}} - \underline{\underline{\sigma}}_0 - \underline{\underline{\sigma}}_1; \quad \underline{\underline{e}}_p \equiv \underline{\underline{e}} - \underline{\underline{e}}_e. \quad (10)$$

Substituting the second relation from (10) into (8) reduces it to the form:

$$\overset{\nabla}{\underline{\underline{b}}} + \underline{\underline{b}} \cdot \underline{\underline{e}}_p + \underline{\underline{e}}_p \cdot \underline{\underline{b}} = \underline{\underline{0}}. \quad (11)$$

Here the operation $\overset{\nabla}{\underline{\underline{b}}}$ has been defined in (5). Note that the form for dissipative strain rate tensor $\underline{\underline{e}}_p$ in (11) has yet to be established.

Substituting (10) into (9) and then in (6) finally yields:

$$TP_s = -q \cdot \underline{\underline{\nabla T}} + tr(\underline{\underline{\sigma}}_p \cdot \underline{\underline{e}}) + tr(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{e}}_p) \quad (\geq 0) \quad (12)$$

The entropy production in (12) has a typical bilinear form $\sum X_k \cdot Y_k$, where $\{X_k\} = \{\underline{\underline{\nabla T}}, \underline{\underline{\sigma}}_p, \underline{\underline{\sigma}}_1\}$ are independent thermodynamic forces of different tensor

dimensionality, and conjugated to them, are the independent quantities, $\{Y_k\} = \{q, \underline{e}, \underline{e}_p\}$, called the thermodynamic fluxes. It should be mentioned that, as in the linear case, the thermodynamic forces and thermodynamic fluxes are chosen to be respectively invariant and skew invariant relative to a reverse time transformation: $t \rightarrow -t$.

Three independent dissipative sources are now clearly seen in (12). The first one is due to the non-isothermal effects reflected by the first term in (12). The remaining contributions represent mechanical dissipation in the system accounted for the second and third terms in (12), which are: (i) the rate of mechanical dissipation produced by work of the irreversible stress $\underline{\sigma}_p$ on the total strain rate \underline{e} , and (ii) the rate of mechanical dissipation produced by work of the viscoelastic stress $\underline{\sigma}_1$ on the irreversible strain rate \underline{e}_p .

In accordance with quasi-linear irreversible thermodynamics, the above thermodynamic forces and fluxes are connected by phenomenological relations, with kinetic coefficients being various tensors that depend on the state variables: temperature T and strains \underline{B} and \underline{b} . Using the arguments of tensor dimensionality and Onsager symmetry of kinetic coefficients, proved for the quasi-linear case by Gyarmati (1970), we can write phenomenological equations in the following general quasi-linear form:

$$\underline{\sigma}_p = \mathbf{M}_1 : \underline{e} - \mathbf{M}_2 : \underline{\sigma}_1; \quad \underline{e}_p = \mathbf{M}_2 : \underline{e} + \mathbf{M}_3 : \underline{\sigma}_1; \quad \mathbf{M}_k = \mathbf{M}_k(T, \underline{B}, \underline{b}); \quad (13)$$

$$\underline{q} = -\underline{\kappa} \cdot \underline{\nabla} T; \quad \underline{\kappa} = \underline{\kappa}(T, \underline{B}, \underline{b}). \quad (14)$$

Here the kinetic coefficients \mathbf{M}_k are some tensors of fourth rank, symmetric in their first and second couples of indices, and in a transposition of the first and second pairs of indices. The tensor \mathbf{M}_1 has the dimensionality of viscosity, while \mathbf{M}_2 is non-dimensional, and \mathbf{M}_3 has the dimensionality of reciprocal viscosity. The scalar products in (13) mean: $(\mathbf{M}_1 : \underline{e})_{ij} \equiv M_{ijkl}^1 e_{lk}$, etc. The heat conductivity $\underline{\kappa}$ is now presented in (14) as a second order symmetric tensor. The dependences of the kinetic tensors in (13) and (14) on the strain tensors \underline{B} and \underline{b} demonstrate the effect of the strain induced anisotropy. The skew Onsager symmetry in constitutive equations (13) is due to the "mixed" nature of constitutive relations between the thermodynamic forces and fluxes we used here for the sake of convenience.

Substituting (13) and (14) into (6) presents the entropy production as the quadratic form,

$$TP_s = tr(\underline{\kappa} \cdot \underline{\nabla} T \underline{\nabla} T) + TR(\mathbf{M}_1 : \underline{e} \underline{e}) + TR(\mathbf{M}_3 : \underline{\sigma}_1 \underline{\sigma}_1) (\geq 0), \quad (15)$$

which due to the second law must be positive definite. Equation (15) means that the second rank tensor $\underline{\kappa}$ and the two four-rank kinetic tensors \mathbf{M}_1 and \mathbf{M}_3 are positive definite, the last two in the sense of a 9×9 matrix whose rows and columns consist of the

terms related to the first and the second pair of indices. No thermodynamic constraint is imposed on the coupling kinetic coefficient $\underline{\underline{M}}_2$ present in the constitutive equations of (13).

The general structure of the rank four kinetic tensors $\underline{\underline{M}}_k$ is quite complicated. Even in the case when they are isotropic tensor functions of a single (symmetric) second rank tensor argument, the explicit structure contains 12 independent constitutive scalars that depend on the three basic invariants of the tensor argument (Leonov, 1987). Although the general structure of tensors $\underline{\underline{M}}_k$ might be established, we avoid here these cumbersome algebraic formulae. Even in the much more simple example of the thermal conductivity tensor $\underline{\underline{\kappa}}(T, \underline{\underline{B}}, \underline{\underline{b}})$ its general structure, established below using the representation theorems (Truesdell and Noll, 1992, p.35), is still quite complicated:

$$\begin{aligned} \underline{\underline{\kappa}}(T, \underline{\underline{B}}, \underline{\underline{b}}) = & \kappa_0 \underline{\underline{\delta}} + \kappa_1 \underline{\underline{B}} + \kappa_2 \underline{\underline{B}}^2 + \kappa_3 \underline{\underline{b}} + \kappa_4 \underline{\underline{b}}^2 + \kappa_5 (\underline{\underline{B}} \cdot \underline{\underline{b}} + \underline{\underline{b}} \cdot \underline{\underline{B}}) \\ & + \kappa_6 (\underline{\underline{B}} \cdot \underline{\underline{b}}^2 + \underline{\underline{b}}^2 \cdot \underline{\underline{B}}) + \kappa_7 (\underline{\underline{B}}^2 \cdot \underline{\underline{b}} + \underline{\underline{b}} \cdot \underline{\underline{B}}^2) + \kappa_8 (\underline{\underline{b}}^2 \cdot \underline{\underline{B}}^2 + \underline{\underline{B}}^2 \cdot \underline{\underline{b}}^2) \end{aligned} \quad (16)$$

Here the nine scalar coefficients κ_i ($i = 0, 1, \dots, 8$) in (16) can depend on temperature T , the six independent invariants, I_j^B and I_j , and on the four mixed independent invariants I_j^{Bb} .

The phenomenological relations in (13) and (14), along with the relations of (4), (5), (10) and (11), represent the closed general set of thermo-rheological nonlinear constitutive relations. In addition to them, one needs to include the balance equations for mass, momentum and internal energy U . Introducing the heat capacity c_d under constant tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$ as $c_d = \partial U / \partial T|_{\underline{\underline{B}}, \underline{\underline{b}}}$, reduces the balance of internal energy to the common heat equation:

$$\rho c_d dT / dt = \underline{\underline{\nabla}} \cdot \underline{\underline{\kappa}} \cdot \underline{\underline{\nabla}} T + tr(\underline{\underline{\sigma}} \cdot \underline{\underline{e}}). \quad (17)$$

In the case of rubber (entropic) elasticity, when $U = U(T)$, the heat capacity is the function of only temperature. Note that the source term $tr(\underline{\underline{\sigma}} \cdot \underline{\underline{e}})$ in the right-hand side of the heat equation (17) is not a mechanical dissipation but a mechanical power (the work per time unit) generated by stresses acting on strain rates.

The above general phenomenological relations include into consideration the Kelvin-Voigt stress. This prevents the "instantaneous" elastic response of viscoelastic solids and liquids caused by an applied stress. Restricting the class of consideration to be solid viscoelasticity admitting an instantaneous response, as solely observed in experiments, results in the simplifications,

$$\underline{\underline{M}}_1 = \underline{\underline{0}}, \quad \underline{\underline{M}}_2 = \underline{\underline{0}}, \quad (18)$$

Relations (18) considerably simplify the above CE's which reduce to the form:

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}^T = \underline{\underline{\sigma}}_0 + \underline{\underline{\sigma}}_1 \quad (\mathbf{M}_1 = \mathbf{0}, \mathbf{M}_2 = \mathbf{0}), \quad \underline{\underline{e}}_p = \mathbf{M}(T, \underline{\underline{B}}, \underline{\underline{b}}) : \underline{\underline{\sigma}}_1 \quad (\mathbf{M} \equiv \mathbf{M}_3) \quad (19)$$

Here the expressions for stresses $\underline{\underline{\sigma}}_0$ and $\underline{\underline{\sigma}}_1$ are given in (4).

Thus the complete set of constitutive relations for viscoelastic solids with instantaneous elasticity consists of (i) elastic constitutive equations that include the first equation in (4) defining the equilibrium (elastic) stress, along with the well-known kinematical equation (5) for the total strain, (ii) the viscoelastic constitutive equations that include the definition of viscoelastic stress in (4), the evolution equation (11) combined with the constitutive relation (19), and (iii) the thermal constitutive relation (16).

3. A simplified model of nonlinear solid viscoelasticity with a single relaxation mode

The general thermodynamic theory for nonlinear behavior of viscoelastic solids developed in the previous Section is too complicated to be used in applications, even in the case of a single nonlinear relaxation mode. Therefore, in this Section some simplifying assumptions are made for our modeling with one nonlinear relaxation mode. These assumptions should be considered as intuitive, as we cannot justify them from any fundamental macroscopic point of view, although they might have some physical reasons, and can also be experimentally verified a posteriori.

The first step is a decoupling of equilibrium and non-equilibrium effects, as has been proposed in (1) and used in the Section 2. The second step is to assume a decoupling of relaxation phenomena from the equilibrium one. Hence we consider the following simplified description of non-equilibrium (relaxations and heat conductivity) effects.

3.1. Simplified modeling of nonlinear relaxation properties

All irreversible properties in the above general theory with instantaneous viscoelasticity are entirely determined by the second stress-strain relation in (4) for the irreversible stress tensor $\underline{\underline{\sigma}}_1$, along with kinetic equation (11) for the evolution of tensor $\underline{\underline{b}}$, and the phenomenological relation (19). Similar to the liquid-like nonlinear viscoelastic theory (Leonov, 1976, 1987, 1999), we assume in the phenomenological relation of (19) that the kinetic tensor \mathbf{M} depends only on temperature and “its own”, non-equilibrium strain tensor $\underline{\underline{b}}$, i.e. $\mathbf{M} = \mathbf{M}(T; \underline{\underline{b}})$. With this assumption, equation (19) becomes:

$$\underline{\underline{e}}_p = \mathbf{M}(T; \underline{\underline{b}}) : \underline{\underline{\sigma}}_1(T; \underline{\underline{b}}) = \underline{\underline{e}}_p(T, \underline{\underline{b}}). \quad (20)$$

Relation (20) means that at a given temperature the non-equilibrium strain rate, $\underline{\underline{e}}_p(T, \underline{\underline{b}})$, is an isotropic tensor function of the non-equilibrium elastic strain tensor $\underline{\underline{b}}$. Then the general structure of the evolution equation (11) for tensor $\underline{\underline{b}}$ is:

$$\overset{\nabla}{\underline{\underline{b}}} + \underline{\underline{\varphi}}(T, \underline{\underline{b}}) = \underline{\underline{0}}; \quad \underline{\underline{\varphi}}(T, \underline{\underline{b}}) \equiv 2 \underline{\underline{b}} \cdot \underline{\underline{e}}_p(T, \underline{\underline{b}}). \quad (11a)$$

This version of the theory has been well developed previously for a single nonlinear relaxation mode in incompressible viscoelastic liquids, when $I_3 = \det \underline{\underline{b}} = 1$. It was then extended for decoupled multi-mode nonlinear modeling with independent tensor parameters, and has been successfully applied to describe nonlinear viscoelastic properties of several polymeric melts employing only a few “nonlinear” numerical parameters (Leonov, 1999). It should be reminded that according to the dissipative inequality (12), $\text{tr}(\underline{\underline{\sigma}}_1 \cdot \underline{\underline{e}}_p) \geq 0$.

3.2. Modeling of nonlinear thermal properties

In spirit of the previous Section, simplifying models for the heat conductivity $\underline{\underline{\kappa}}$ could be suggested so that the thermal conductivity tensor in (16) depends only on equilibrium strain $\underline{\underline{B}}$ or on the non-equilibrium elastic strain $\underline{\underline{b}}$. However, a dependence of $\underline{\underline{\kappa}}$ on $\underline{\underline{b}}$ predicts an isotropic thermal conductivity in the equilibrium under stress, which contradicts experimental data (see Novichionok and Shulman, 1971). Another possibility is a dependence of $\underline{\underline{\kappa}}$ on the full strain $\underline{\underline{B}}$, i.e.

$$\underline{\underline{\kappa}}(T, \underline{\underline{B}}) = \kappa_0 \underline{\underline{\delta}} + \kappa_1 \underline{\underline{B}} + \kappa_2 \underline{\underline{B}}^2 ; \quad \kappa_i = \kappa_i(T; I_1^B, I_2^B, I_3^B). \quad (21)$$

Here the second rank tensor $\underline{\underline{\kappa}}$ is an isotropic tensor function of the total elastic Finger deformation $\underline{\underline{B}}$. Note that equation (21) predicts that after unloading the heat conductivity is isotropic. Therefore a crucial test of (21) is measuring heat conductivity during a retardation experiment, viz. after unloading.

4. Fractioning the compressible (bulk) and shearing effects, and simplifications

We now analyze compressibility effects within the above viscoelastic approach with instantaneous elasticity, considering initially the pure elastic compressible case, and then the viscoelastic effects. The main idea here is to introduce instead of invariants I_k^B , the density ρ and other corresponding invariants as the new independent variables. This approach originates from a specific equilibrium stress-strain relation (see equation (27) below in the text), which in simple elongation has been first introduced by Flory (1961) (see also Treloar, 1975), and in the 3D elastic case, by Leonov (1976). We then will generalize these results for finite viscoelasticity. A lot of direct attempts to treat compressibility in finite (thermo-) elasticity using the general form for free energy function, $F = F^0(T; I_1^B, I_2^B, I_3^B)$, have also been considered in the literature (e.g. see Anand, 1996, and references there). However, using these results, it is difficult to separate bulk and shear deformations.

4.1. Equilibrium (pure elastic) case

Here the free energy is represented in the form: $F = F^0(T; I_1^B, I_2^B, I_3^B)$, the stress tensor is represented by the first formula in (4), and the kinematical relation is given by (5). Additionally, there are two well-known equations, one relating the invariant I_3 and density ρ , and the second, the mass balance equation:

$$I_3^B = (\rho_0 / \rho)^2, \quad \partial_t \rho + \nabla \cdot (\rho \underline{u}) = 0 \quad \text{or} \quad d \ln \rho / dt = -\text{tr} \underline{e}. \quad (22)$$

Here \underline{u} is the velocity vector. Note that the second relation in (22) is easily derived from the first one and the kinematical relation (5). Keeping in mind that the invariants I_j^B occur in the Hamilton-Cayley identity,

$$\underline{\underline{B}}^3 - I_1^B \underline{\underline{B}}^2 + I_2^B \underline{\underline{B}} - I_3^B \underline{\underline{\delta}} = \underline{\underline{0}}, \quad (23)$$

we introduce new tensor $\hat{\underline{\underline{B}}}$,

$$\hat{\underline{\underline{B}}} = (I_3^B)^{-1/3} \underline{\underline{B}} \equiv (\rho / \rho_0)^{2/3} \underline{\underline{B}}, \quad (24)$$

and the corresponding basic invariants \hat{I}_j^B ,

$$\begin{aligned} \hat{I}_1^B &\equiv \text{tr} \hat{\underline{\underline{B}}} = (\rho / \rho_0)^{2/3} I_1^B, \quad \hat{I}_3^B = 1 \\ \hat{I}_2^B &\equiv 1/2[(\hat{I}_1^B)^2 - \text{tr} \hat{\underline{\underline{B}}}^2] = \text{tr} \hat{\underline{\underline{B}}}^{-1} = (\rho / \rho_0)^{4/3} I_2^B. \end{aligned} \quad (25)$$

Formulae (24) and (25) reduce the Hamilton-Cayley identity (23) to the “incompressible” form:

$$\hat{\underline{\underline{B}}}^3 - \hat{I}_1^B \hat{\underline{\underline{B}}}^2 + \hat{I}_2^B \hat{\underline{\underline{B}}} - \underline{\underline{\delta}} = \underline{\underline{0}}. \quad (23a)$$

Using (25), the basic invariants I_j^B in the equilibrium part $F^0(T; I_1^B, I_2^B, I_3^B)$ of the free energy can be expressed via the density ρ and the two new invariants \hat{I}_1^B and \hat{I}_2^B to obtain:

$$F^0(I_1^B, I_2^B, I_3^B) = F^0(\hat{I}_1^B (\rho_0 / \rho)^{2/3}, \hat{I}_2^B (\rho_0 / \rho)^{4/3}, (\rho_0 / \rho)^2) \equiv \hat{F}^0(\rho, \hat{I}_1^B, \hat{I}_2^B). \quad (26)$$

The temperature in (26) has been omitted for the sake of simplicity. Formula (26) allows expressing the equilibrium stress-strain relation in the form:

$$\begin{aligned} \underline{\underline{\sigma}}_0 &= -\rho^2 \hat{F}_\rho^0 \underline{\underline{\delta}} + 2\rho [\hat{F}_1^0 (\hat{\underline{\underline{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0 (\hat{\underline{\underline{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})] \\ &(\hat{F}_\rho^0 = \partial \hat{F}^0 / \partial \rho, \quad \hat{F}_1^0 = \partial \hat{F}^0 / \partial \hat{I}_1^B, \quad \hat{F}_2^0 = \partial \hat{F}^0 / \partial \hat{I}_2^B). \end{aligned} \quad (27)$$

The first term in (27) represents the equilibrium thermodynamic pressure, and the second deviatoric term reflects the effects of isochoric ("shearing") deformations. When the (infinitesimal) bulk modulus K is extremely high, as compared to the infinitesimal shear (Hook) modulus G , the first term can be considered as "isotropic pressure", with the formal limit: $p = \lim \rho^2 \hat{F}_\rho \big|_{\Delta\rho \rightarrow 0, K \rightarrow \infty}$.

Finally, using relations (24) reduces the kinematical equation (5) to the form:

$$\underline{\underline{\hat{B}}} \equiv \underline{\underline{\hat{B}}} - \underline{\underline{\hat{B}}} \cdot \underline{\underline{\hat{e}}} - \underline{\underline{\hat{e}}} \cdot \underline{\underline{\hat{B}}} = \underline{\underline{0}} ; \quad \underline{\underline{\hat{e}}} \equiv \underline{\underline{e}} - 1/3 \underline{\underline{\delta}} \text{tr} \underline{\underline{e}} = \underline{\underline{e}} - 1/3 \underline{\underline{\delta}} \rho^{-1} d\rho / dt . \quad (28)$$

Here $\underline{\underline{\hat{e}}}$ is the deviator of the strain-rate tensor $\underline{\underline{e}}$. Comparing (5) and (28) demonstrates that the kinematical relation (5) is invariant relative to the volume "compressible-isochoric" transformation: $\underline{\underline{B}} \rightarrow \underline{\underline{\hat{B}}}$, $\underline{\underline{e}} \rightarrow \underline{\underline{\hat{e}}}$.

4.2. Non-equilibrium (viscoelastic) case

In this case, the component $F^1 = F^1(T; I_1, I_2, I_3)$ of the free energy function is used instead of the above equilibrium one, F^0 . Still, the way of the analysis here is quite similar to that for the equilibrium case. Similar to the first relation in (22), we now introduce a new irreversible ("density-like") variable ρ^i as:

$$\rho^i / \rho_0 = I_3^{-2} . \quad (29)$$

Relation (29) takes into account the fact that in equilibrium, $\rho_o^i = \rho_0$. Then similarly to (24) and (25), we introduce the new hidden ("incompressible") tensor variable $\underline{\underline{\hat{b}}}$ and its invariants \hat{I}_j as:

$$\underline{\underline{\hat{b}}} = (I_3)^{-1/3} \underline{\underline{b}} \equiv (\rho^i / \rho_0)^{2/3} \underline{\underline{b}} , \quad (30)$$

$$\hat{I}_1 \equiv \text{tr} \underline{\underline{\hat{b}}} = (\rho^i / \rho_0)^{2/3} I_1 , \quad \hat{I}_3 = 1 \quad (31)$$

$$\hat{I}_2 \equiv 1/2[(\hat{I}_1)^2 - \text{tr} \underline{\underline{\hat{b}}}^2] = \text{tr} \underline{\underline{\hat{b}}}^{-1} = (\rho^i / \rho_0)^{4/3} I_2 .$$

Relations (29)-(31) reduce the Hamilton-Cayley identity for tensor $\underline{\underline{b}}$ to the "incompressible" form:

$$\underline{\underline{\hat{b}}}^3 - \hat{I}_1 \underline{\underline{\hat{b}}}^2 + \hat{I}_2 \underline{\underline{\hat{b}}} - \underline{\underline{\delta}} = \underline{\underline{0}} . \quad (32)$$

Then similar to (26), one can represent the irreversible part of the free energy in the form, $F^1(T, I_1, I_2, I_3) = \hat{F}^1(T, \rho^i, \hat{I}_1, \hat{I}_2)$, and obtain, similar to (27), the formulae for stress in the irreversible case:

$$\underline{\underline{\sigma}} = -p^T \underline{\underline{\delta}} + \underline{\underline{\hat{\sigma}}}; \quad p^T = p_0 + p_1; \quad \underline{\underline{\hat{\sigma}}} = \underline{\underline{\hat{\sigma}}}_0 + \underline{\underline{\hat{\sigma}}}_1. \quad (33)$$

Here p^T is the thermodynamic pressure due to compressibility of the viscoelastic solid, with equilibrium p_0 and non-equilibrium p_1 components, presented as:

$$p_0 = \rho^2 \partial \hat{F} / \partial \rho, \quad p_1 = \rho \rho^i \partial \hat{F} / \partial \rho^i. \quad (34)$$

The tensor variable $\underline{\underline{\hat{\sigma}}}$ in (33) is the thermodynamic stress deviator consistent of two, equilibrium $\underline{\underline{\hat{\sigma}}}_0$ and non-equilibrium $\underline{\underline{\hat{\sigma}}}_1$, deviator components. These are of the form:

$$\begin{aligned} \underline{\underline{\hat{\sigma}}}_0 &= 2\rho [\hat{F}_1^0(\underline{\underline{\hat{B}}} - 1/3 \hat{I}_1^B \underline{\underline{\delta}}) - \hat{F}_2^0(\underline{\underline{\hat{B}}}^{-1} - 1/3 \hat{I}_2^B \underline{\underline{\delta}})] \\ \underline{\underline{\hat{\sigma}}}_1 &= 2\rho [\hat{F}_1^1(\underline{\underline{\hat{b}}} - 1/3 \hat{I}_1 \underline{\underline{\delta}}) - \hat{F}_2^1(\underline{\underline{\hat{b}}}^{-1} - 1/3 \hat{I}_2 \underline{\underline{\delta}})]. \end{aligned} \quad (35)$$

To derive the evolution equation for the bulk irreversible parameter ρ^i , the kinetic equation (11) is contracted (right or left) with tensor $\underline{\underline{b}}^{-1}$ to obtain:

$$d \ln I_3 / dt + 2 \text{tr} \underline{\underline{e}}_p = 2 \text{tr} \underline{\underline{e}}. \quad (36a)$$

Using (29) and the last relation in (22) reduces (36a) to another form:

$$d \ln \rho^i / dt - \text{tr} \underline{\underline{e}}_p = d \ln \rho / dt = -\text{tr} \underline{\underline{e}}. \quad (36b)$$

Equations (36a,b) show that the difference between ρ^i and ρ vanishes in the equilibrium limit when $\underline{\underline{e}}_p \rightarrow 0$. To close the set of bulk kinetic equations, one should complement equations (36a,b) with the phenomenological relation (20) or (11a). Finally, substituting (36b) into (11) reduces relation (11) to the “incompressible” form:

$$\underline{\underline{\hat{b}}} - \underline{\underline{\hat{b}}} \cdot \underline{\underline{\hat{e}}} - \underline{\underline{\hat{e}}} \cdot \underline{\underline{\hat{b}}} + \underline{\underline{\hat{b}}} \cdot \underline{\underline{\hat{e}}}_p + \underline{\underline{\hat{e}}}_p \cdot \underline{\underline{\hat{b}}} = 0. \quad (37)$$

Here $\underline{\underline{\hat{b}}}$ is defined in (30), with $\underline{\underline{\hat{e}}}$ and $\underline{\underline{\hat{e}}}_p$ being the respective deviators of $\underline{\underline{e}}$ and $\underline{\underline{e}}_p$.

4.3. Simplifications: decoupling of bulk and shearing effects

In rubberlike materials, the bulk effects are usually insignificant when compared with the huge shearing deformations. Therefore one can attempt to completely decouple bulk and shear effects in viscoelastic deformations and stresses, which leads to a big simplification in the constitutive equations for finite viscoelasticity. There is a warning, however, whereas the bulk deformations insignificantly affect the shear strains, the contrary may not be true. There is a need for experimental verification of the simplifying formulae proposed below.

The first step to take in the simplification is the assumption of fractioning the free energy into a sum of bulk and shearing terms,

$$F = F_b + F_{sh}, \quad (38)$$

where

$$F_b = F_b^0(T, \rho) + F_b^1(T, \rho^i), \quad F_{sh} = F_{sh}^0(T, \hat{I}_1^B, \hat{I}_2^B) + F_{sh}^1(T, \hat{I}_1, \hat{I}_2). \quad (39)$$

With respect to (38) and (39), the formulae of (34) and (35) show that a decoupling of bulk and shear phenomena happen for both equilibrium and non-equilibrium parts of the stress tensor.

The second step to take in the simplification is the assumption of a decoupling of the bulk and shear evolution equations (36) and (37). In this regard, we assume:

$$tr \underline{\underline{e}}_p = -\alpha(\rho^i) p_1(T, \rho^i) / \theta_b^1(T) = -[\alpha(\rho^i) / \theta_b^1(T)] \rho \rho^i \partial \hat{F}_b^1 / \partial \rho^i(T, \rho^i), \quad (40)$$

$$\underline{\underline{e}}_p = \underline{\underline{e}}_p(T, \underline{\underline{b}}) = 1/4[\beta(\hat{I}_1, \hat{I}_2) / \theta_1(T)] \cdot [\underline{\underline{b}} - \underline{\underline{b}}^{-1} - 1/3(\hat{I}_1 - \hat{I}_2)\underline{\underline{e}}]. \quad (41)$$

Formulae (33)-(35) and (38)-(41) present the possible complete decoupling of bulk and shear viscoelastic phenomena. Note that formula (41) for the deviator $\underline{\underline{e}}_p$ has been taken in the form as proposed and tested for polymer fluids and a gum rubber (Leonov, 1999; Mitra, 2000). The temperature dependent parameters $\theta_b^1(T)$ and $\theta_1(T)$ are the bulk and shear relaxation times, which, as shown in the next Section, occur in linear viscoelasticity. Due to the second law, the functions $\alpha(\rho^i)$ and $\beta(\hat{I}_1, \hat{I}_2)$ are positive and they go to the unity in the equilibrium limit ($\rho^i \rightarrow \rho_0$, $\hat{I}_1 \rightarrow \hat{I}_2 \rightarrow 3$). They represent strain scaling factors for the corresponding relaxation times. These scaling factors are similar to the “material clock” introduced in the K-BKZ theory by Bernstein and Shokooh (1980), following the initial approach developed in viscoplasticity by Valanis (1971).

Substituting (40) into (36b) yields the nonlinear bulk (scalar) evolution equation:

$$d \ln \rho^i / dt + [\alpha(\rho^i) / \theta_b^1(T)] \rho \rho^i \partial \hat{F}_b^1 / \partial \rho^i(T, \rho^i) = d \ln \rho / dt. \quad (42)$$

Substituting (41) into (37) produces the nonlinear tensor evolution equation:

$$\hat{\underline{\underline{b}}} - \hat{\underline{\underline{b}}} \cdot \hat{\underline{\underline{e}}} - \hat{\underline{\underline{e}}} \cdot \hat{\underline{\underline{b}}} + 1/2[\beta(\hat{I}_1, \hat{I}_2)/\theta_1(T)] \cdot [\hat{\underline{\underline{b}}}^2 - 1/3(\hat{I}_1 - \hat{I}_2)\hat{\underline{\underline{b}}} - \underline{\underline{\delta}}] = \underline{\underline{0}}. \quad (43)$$

The evolution equations in (42) and (43) are complemented by the stress-strain relations of (33)-(35) with account for (38) and (39). This is a complete set of nonlinear constitutive equations with a decoupling in the equilibrium and non-equilibrium, and also in the bulk and shearing, phenomena.

4.4. Limit to linear viscoelasticity

We demand that the nonlinear set of CE's derived above should have a regular limit to linear viscoelasticity, including linear elasticity. The common formulae

$$\underline{\underline{B}} = \exp(2\underline{\underline{h}}_0); \quad \underline{\underline{b}} = \exp(2\underline{\underline{h}}_1) \quad (44)$$

are used below to relate the Finger strain tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$, and the respective Hencky strain tensors, $\underline{\underline{h}}_0$ and $\underline{\underline{h}}_1$. Then for small Hencky strains, the strain tensors $\underline{\underline{B}}$ and $\underline{\underline{b}}$ can be presented as:

$$\underline{\underline{B}} \approx \underline{\underline{\delta}} + 2\underline{\underline{h}}_0 \quad (|\underline{\underline{h}}_0| \ll 1); \quad \underline{\underline{b}} \approx \underline{\underline{\delta}} + 2\underline{\underline{h}}_1 \quad (|\underline{\underline{h}}_1| \ll 1). \quad (45)$$

Also, with the precision of the higher terms,

$$I_1^B = I_2^B \approx 3 + tr(\underline{\underline{h}}_0^2), \quad I_3^B \approx 1 + tr \underline{\underline{h}}_0; \quad I_1 = I_2 \approx 3 + tr(\underline{\underline{h}}_1^2), \quad I_3^B \approx 1 + tr \underline{\underline{h}}_1, \quad (46)$$

where

$$tr \underline{\underline{h}}_0 \approx -\Delta\rho / \rho_0; \quad tr \underline{\underline{h}}_1 \approx -\Delta\rho^i / \rho_0. \quad (47)$$

Substituting these formulae into the general expression for the Helmholtz potential $F = F^0(T; I_1^B, I_2^B, I_3^B) + F^1(T; I_1, I_2, I_3)$, expanded in a Taylor series about the unloaded state yields, with the precision not higher than the quadratic, the following presentation:

$$\Delta F \approx 1/2 K_0(T) (tr \underline{\underline{h}}_0)^2 + 1/2 G_0(T) tr(\underline{\underline{h}}_0^2) + 1/2 K_1(T) (tr \underline{\underline{h}}_1)^2 + 1/2 G_1(T) tr(\underline{\underline{h}}_1^2). \quad (48)$$

The first two terms in (48) represent the equilibrium contribution to the free energy, while the second two terms represent the non-equilibrium one, vanishing in equilibrium. Here K_0 and K_1 are the equilibrium and non-equilibrium bulk moduli; G_0 and G_1 are the

equilibrium and non-equilibrium shear (Hookean) moduli; $\hat{\underline{h}}_0$ and $\hat{\underline{h}}_1$ denote the respective deviators of equilibrium and non-equilibrium, infinitesimal, Hencky strain tensors. Equations (33)-(35) hold here with respective elastic and viscoelastic stress-strain relations being of the form:

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}_0 + \underline{\underline{\sigma}}_1; \quad \underline{\underline{\sigma}}_0 = K_0 \cdot (tr \underline{\underline{h}}_0) \underline{\underline{\delta}} + G_0 \hat{\underline{h}}_0; \quad \underline{\underline{\sigma}}_1 = K_1 \cdot (tr \underline{\underline{h}}_1) \underline{\underline{\delta}} + G_1 \hat{\underline{h}}_1, \quad (49)$$

while the evolution equations (42) and (43) take their respective forms:

$$\begin{aligned} d(tr \underline{\underline{h}}_0) / dt &= tr \underline{\underline{e}}, \quad d\hat{\underline{h}}_0 / dt = \hat{\underline{e}}; \\ d(tr \underline{\underline{h}}_1) / dt + (tr \underline{\underline{h}}_1) / \theta_1^b &= tr \underline{\underline{e}}, \quad d\hat{\underline{h}}_1 / dt + \hat{\underline{h}}_1 / \theta_1 = tr \hat{\underline{e}}. \end{aligned} \quad (50)$$

For shearing components of the infinitesimal tensors, these equations coincide with those that have been considered for linear viscoelasticity with a single relaxation mode in the first paper (Freed and Leonov, 2002) of this series.

Finally, it should be mentioned that in the linear limit, the heat capacity tensor $\underline{\underline{\kappa}}$ degenerates into an isotropic tensor (i.e. scalar): $\underline{\underline{\kappa}} \rightarrow \kappa_0 \underline{\underline{\delta}}$.

5. Simplified models of solid viscoelasticity with several nonlinear relaxation modes

We now consider multi-mode, nonlinear, solid-like viscoelasticity. In order to do that in a constructive way, we adopt all the modeling simplifications as discussed in the previous Sections 3 and 4 for a nonlinear, single relaxation mode. We will also additionally use, for both the shearing θ_k and bulk θ_k^b relaxation times, the inequalities:

$$\theta_k(T) \gg \theta_{k+1}(T); \quad \theta_k^b(T) \gg \theta_{k+1}^b(T). \quad (51)$$

Inequalities (51) allow us to present the properties of viscoelastic solids as the sum of nonlinear viscoelastic properties for independent relaxation modes. Several types of additivities are involved here: (i) the additivity of elastic and viscoelastic nonlinear strains; (ii) the additivity of various viscoelastic nonlinear modes, and (iii) the additivity of shearing and bulk (compressible) viscoelastic properties within various nonlinear modes. In this approach, the Helmholtz free energy function is represented in the form:

$$\begin{aligned} F &= F^0(T; I_j^B) + \sum_{k=1}^n F^k(T; I_j^k) = F_b^0(T; \rho) + F_{sh}^0(T; \hat{I}_1^B, \hat{I}_2^B) \\ &\quad + \sum_{k=1}^n [(\rho_k^i / \rho_0) F_b^k(T; \rho_k^i) + F_{sh}(T; \hat{I}_1^k, \hat{I}_2^k)]. \end{aligned} \quad (52)$$

Correspondingly, the stress in the system is represented as:

$$\begin{aligned}\underline{\underline{\sigma}} = \underline{\underline{\sigma}}_0(T, \underline{\underline{B}}) + \sum_{k=1}^n \underline{\underline{\sigma}}_k(T; \underline{\underline{b}}_k) = -p_0(T, \rho) \underline{\underline{\delta}} + \hat{\underline{\underline{\sigma}}}_0(T, \hat{\underline{\underline{B}}}) \\ + \sum_{k=1}^n [-p_k(T, \rho_k^i) \underline{\underline{\delta}} + \hat{\underline{\underline{\sigma}}}_k(T, \hat{\underline{\underline{b}}}_k)].\end{aligned}\quad (53)$$

Here the “pressures”, P_0, P_1, \dots, P_n and stress deviators, $\hat{\underline{\underline{\sigma}}}_0, \hat{\underline{\underline{\sigma}}}_1, \dots, \hat{\underline{\underline{\sigma}}}_n$, are defined by formulae (34) and (35).

Additionally, in the evolution equations (42) and (43) for non-equilibrium quantities, the scalars ρ_k^i and tensors $\hat{\underline{\underline{b}}}_k$ are used. Thus the relations (34), (35), (52), (53) and (42), (43) form a closed set of nonlinear constitutive equations of the differential type. These equations can model the properties of both the liquid and solid states of rubbery materials, with changing parameters during a cure reaction. The nice feature of these equations is that they have the same structure, except for the equilibrium part.

Additional assumptions and simplifications could be considered that allow for various scaling approaches.

(i) *Temperature scaling*

There is a fundamental reason related to the physics of rubber elasticity (Treloar, 1975; Ferry, 1980) to assume that both the equilibrium and non-equilibrium shearing strain energies in equation (52) are simply proportional to the absolute (Kelvin) temperature, T . Therefore both the equilibrium and non-equilibrium shearing stresses in equation (53) will be proportional to ρT , too. We can also assume that all the relaxation times in our discrete spectrum for shear viscoelasticity have the same temperature dependence as $\theta_1(T)$, say a WLF representation above the glass transition, or an Arrhenius form for those temperatures well above the glass transition. Then scaling the stresses with ρT and time with $\theta_1(T)$, makes the shearing terms in the viscoelastic CE's temperature independent. This is the *time-temperature superposition* principle applied to nonlinear viscoelastic shearing phenomena. Likewise scaling for the bulk relations might also be correct. Although the bulk relaxation times $\theta_k^b(T)$ may have a uniform temperature dependence, it might be different from that for shearing. Therefore, in general, time-temperature superposition can work separately for shearing and bulk phenomena, but might be violated when considering a combined, bulk-shearing deformation. Experimental verification of this situation is important here.

(ii) *Deformation Scaling*

If the non-dimensional (numerical) material parameters, involved in the modeling of nonlinear terms in the thermodynamic equation for stress and deformation kinetics, are independent of relaxation mode, then the nonlinear behavior in the relaxation modes is self-similar. Consequently, a scaling approach can be effectively used in advanced computations to restore the values for various modes from calculations made for a single

relaxation mode. The analysis of this type of scaling has been made for viscoelastic liquids by Leonov and Padovan (1999).

6. Conclusion

The present, second, paper of this series is devoted to derivation of CE's for non-isothermal solid viscoelasticity with finite and, in general, compressible deformations (the first paper by Freed and Leonov, 2002, analyzed the linear theory). We employed here the general approach of quasi-linear, non-equilibrium thermodynamics that has been successfully used and tested by Leonov and his collaborators (1976, 1987, 1999) for viscoelastic liquids. Several assumptions were employed here to present the results of the constitutive theory in its most simplified form.

First, we assumed that the total free energy could be decomposed in a sum of equilibrium and non-equilibrium terms. Although this decomposition is the only one used in other theoretical approaches, there is no justification for making this assumption.

Second, we assumed that the non-equilibrium viscoelastic properties could be represented as a sum of independent nonlinear relaxation modes, originated from their linear modes. This crucial simplifying assumption has successfully been used for liquid-like nonlinear viscoelasticity (Leonov, 1976, 1987, 1999) when the relaxation times in a discrete relaxation spectrum are well separated. Using a Pade-Laplace technique (Simhambhatla and Leonov, 1993) for effective discretization of relaxation spectrum from experimental data, it was additionally showed (e.g. see Leonov, 1999) that this assumption is always satisfied for polymer melts and concentrated polymeric solutions. Thus the presented approach essentially views the nonlinear viscoelastic effects in solids as similar to these found in the liquids. For cross-linked rubbers, this approach has been experimentally confirmed by chemo-rheological studies (e.g. see Mitra, 2000). In these studies, the changes in viscoelastic (and occurrence of equilibrium, elastic) parameters in the course of vulcanization were detected experimentally and modeled.

Third, we also fractioned, and then completely decoupled the shearing and bulk (compressibility) elastic and viscoelastic phenomena in nonlinear solid viscoelasticity. Although the fractioning of bulk and shearing effects is based on the fundamental introduction of new strain variables, the simplified decoupling of these effects is by no means fundamental and needs experimental testing.

Finally, the quasi-linear thermodynamic approach we employed automatically predicts the strain-induced anisotropy in heat conductivity, which has been detected experimentally in equilibrium under large strains in crosslinked rubbers (Novichionok and Shulman, 1971).

It should be mentioned that before the proposed constitutive theory can be used, one needs to specialize some material functions, such as the functional forms of the equilibrium and non-equilibrium free energy functions, etc, along with some stability constraints imposed on these. This will be done in the next, final paper of the series.

We conclude by mentioning that the results presented in this paper are valid for rubbery region of nonlinear solid viscoelasticity. A complementary approach for the glassy region will be presented in the next paper.

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